

EFFECTS OF EVAPORATION/CONDENSATION ON SPREADING AND CONTACT ANGLE OF A VOLATILE LIQUID DROP

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ABSTRACT

Effects of evaporation/condensation on spreading and contact angle were experimentally studied. A sessile drop of R-113 was tested at different vapor environments to determine the effects of evaporation/condensation on the evolution of contact diameter and contact angle of the drop. Condensation on the drop surface occurs at both the saturated and a nonsaturated vapor environments and promotes the spreading. When the drop is placed in the saturated vapor environment it tends to completely wetting and spreads rapidly. In a nonsaturated vapor environment, the evolution of the sessile drop is divided three stages: condensation-spreading stage, evaporation-retracting stage and rapid contracting stage. In the first stage the drop behaves as in the saturated environment. In the evaporation-retracting stage, the competition between spreading and evaporation of the drop determines the evolution characteristics of the contact diameter and the contact angle. A lower evaporation rate struggles against the spreading power to turn the drop from spreading to retracting with a continuous increase of the contact angle. The drop placed in open air has a much higher evaporation rate. The strong evaporation suppresses the spreading and accelerates the retraction of the drop with a linear decrease of the contact diameter. The contraction of the evaporating drops is gradually accelerated when the contact diameter decreases to 3 mm and less till drying up, though the evaporation rate is gradually slowing down.

Keywords: Spreading, contact angle, evaporation, condensation

INTRODUCTION

The spreading of a liquid on a solid surface occurs in many practical processes. The most common example in our daily life is the spreading of water droplets on a glass plate, such as raindrops on a glass window. The applications in technological and biological process include tertiary oil recovery, painting, coating, soldering, gluing, lubrication, mould filling, film cooling, boiling heat transfer, and biological cell interactions. It is also concerned by the engineers working with the performance of fuel tanks in Space.

The spreading of a liquid on a solid surface is also a fundamental problem in fluid mechanics. The motion of the liquid during the spreading process exemplifies the general problem of moving contact lines. As pointed out by Benintendi and Smith [1], the main modeling difficulties stem from the fact that the exact physics governing the fluid behavior in this microscope region is unknown. Dussan [2] and De Gennes [3] have reviewed the importance of the problem and the difficulties of the modeling. Spreading of nonvolatile liquid droplets on a horizontal solid surface is a simple and useful tool in the study of the free-boundary problem, and therefore has been well studied by many investigators. A comprehensive review was made by Leger and Joanny [4]. The lack of volatility of the liquid implies the conservation of mass and volume, and thus simplifies the theoretical analysis. However, the occurrence of evaporation of common liquids is inevitable as long as the environment in the close vicinity of the droplet is not saturated with the vapor of the liquid. A well understanding of the evaporation influences on the contact angle of the droplet in controlled environment conditions is important in the study of the spreading. Unfortunately, both experimental and theoretical studies on this subject are scarce for the difficulty in accurate measurements and lack of appropriate theoretical method to handle.

Recently, Anderson and Davis [5] analytically studied spreading of a two-dimensional volatile liquid droplet on a uniformly heated horizontal surface using lubrication theory. Hocking [6] considered that the macroscopic contact angles deviates from the microscopic angle in slip region and found that the contact angle is increased by evaporation.

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There are many contradictions in the results of the available studies. For example, Shanahan and Bourges [7, 8] concluded that evaporation from the liquid drop meniscus will lower the contact angle, but Moosman and Homsy [9], and Sujanani and Wayner [10] reported an increase in the contact angle when evaporation is present. Marangoni flow found in Anderson and Davis' study is directly opposite from the observations in Cazabat et al. [11] and Redon et al. [12]. Obviously, both further theoretical and experimental studies using appropriate techniques are needed to clear the dominant mechanism in the evaporating drop, especially near the contact line region.

The most common method to measure the contact angle, the contact radius, and the height of a sessile drop on a solid surface is to view the drop from its edge through an optical microscope. This method can give only local information in the view direction. Zhang and Yang [13, 14] developed a laser shadowgraphy method to investigate the evaporation of sessile drop on a glass plate. The whole periphery of the drop can be tested simultaneously and the instantaneous drop size, including the contact diameter, the maximum height of the drop, and volume-time history can be determined. Allain et al. [15] used the same method to measure the contact angle of sessile drops. As basic key parameters, the drop diameter and the refracted image of the drop were measured simultaneously on the screen. A considerable large error resulted from the fuzzy outer rim of the projected shadow of the drop for the diameter of the drop is only an order of 1 mm. This problem becomes more serious for the volatile liquid sessile drops when its base diameter contracts rapidly due to the evaporation. Based on the laser shadowgraphy method developed by Zhang and Yang, we suggested a new optical arrangement to measure the contact angle and the evaporation rate of a sessile drop with much higher accuracy [16].

As it is well known that R-113 ($C_2Cl_3F_3$) is a highly-wetting dielectric fluid and was widely used as the working fluid for boiling heat transfer investigations, which thermophysical properties can be found in reference [17]. The study of the spreading of R-113 on a solid surface would contribute to well understanding of the re-wetting mechanism in the nucleate boiling heat transfer. It is also a good test liquid sample for the experimental study of the spreading of a volatile liquid on a solid surface for its low dielectric constant, which was found to have a considerable influence on the drop stability [13].

The present study focuses attention on the effects of evaporation/condensation on the spreading process and the evolution of the contact angle of R-113 on a glass plate. A sessile drop of R-113 was tested at different vapor environments to determine the effects of evaporation on the spreading characteristics and the time-history of the contact angle.

EXPERIMENTAL APPARATUS

Laser shadowgraphy and direct photography were simultaneously achieved by using a hybrid optical arrangement. The apparatus consisted of a laser light, a white light, a collimator, two beam splitters, two video recording systems (each constituted by a CCD zoom camera with a relevant video recorder and a monitor), a test section, an aluminized mirror, and a screen, as shown in Fig. 1. Uniphase Model 1105p, 10-mW cylindrical helium-neon laser and Olympus Model Highlight 2000 were used as the laser light source and the white light source, respectively. Both the lights passed through the collimator, Newport Model LC-075, via the beam splitter I, and were collimated to parallel beams coincidentally. The beam splitter II was used to reflect the two parallel beams without obstructing of top view of the tested sessile drop, which was recorded by the video recording system I with a 10x of magnification. The recording system II recorded the drop refractive image projected on the screen, on which a vertical ruler and a horizontal ruler were marked across the center. The two recorders were controlled synchronously. The test section was made of a microscope glass slides and four pieces of plastic plate. The four plastic plates, 3 mm thick and 20 mm wide, were glued on a 1 mm thick microscope glass slide of 75 x 50 mm to form a rectangular pan. Two liquid reservoirs of 44 x 10 x 10 mm, made of copper, were placed in the pan against the sidewalls. For the experiment of the drop spreading in the saturated vapor environment, using another 1 mm thick rectangular microscope glass slide of 75 x 50 mm to cover the test section, sealed with Dow Corning high vacuum grease to form a hermetic box. The two glass slides were adjusted to parallel each other enabling the parallel lights passing through the drop vertically and the drop being viewed from top without distortion. In order to create a nonsaturated vapor environment three pieces of 1 mm thick microscope glass slides were used to constitute the cover. One, 75 x 25 mm, was used as the main cover and fixed at the middle of the test section with the vacuum grease, which was adjusted to parallel with the bottom of the test section. Two slides, 75 x 12.5 mm each, were placed at the both sides of the main cover and can be slid laterally to function as a shutter to control the opening of the cover. A 25 μ l Hamilton microsyringe was inserted in the test section along a slideway predrilled on a sidewall of the test section to deposit the drop. The parallel laser beam was used to produce a refracted image of the sessile drop with interference fringes on the screen. From the image, one can obtain important information related to the contact angle through the measuring of the diameter of the outmost fringe ring. The white light beam is used to get sharper photograph of the top view of the sessile drop, which has no influence on the laser shadowgraphy. The aluminized mirror was mounted at 45 degree to obtain a horizontal view of the image refracted by the drop.

Before each experiment, the bottom surface of the test section was cleaned by ethanol and wiped by Olympus lens cleaning tissues. Then the test section was covered by a soft tissue and shelved in open air at least 24 hours during which the bottom surface became free of residual liquid molecules while remaining intact from impurity in the ambient air.

Drops of R-113, one per experiment, varying from $2.5 \mu\text{l}$ to $5 \mu\text{l}$ were deposited on the bottom of the test section using the microsyringe. The evaporation environment of the drop was controlled through the liquid reservoir and the shutter plates. Three typical evaporation environments of the sessile drop were tested: the saturated environment of R-113 vapor, a nonsaturated environment of R-113 vapor, and the open air. In order to obtain the saturated or a nonsaturated vapor environment, 30 ml liquid of R-113 of volume was injected into the reservoirs of the test section and the test section was covered by the cover slide and sealed with Dow Corning high vacuum grease. Then the hermetic box was laid aside for at least 30 minutes to obtain the saturated vapor environment of the test section. The shutter plates can be partially open to obtain a nonsaturated vapor environment. For the cases of the drop evaporating in open air, just let the test section uncovered. It should be noted that the evaporation/condensation rate of the sessile drop varies with the vapor environment and dramatically affects the spreading characteristics of the drop, which is our major concern. Therefore, we measured the evaporation/condensation rate rather than the saturation level.

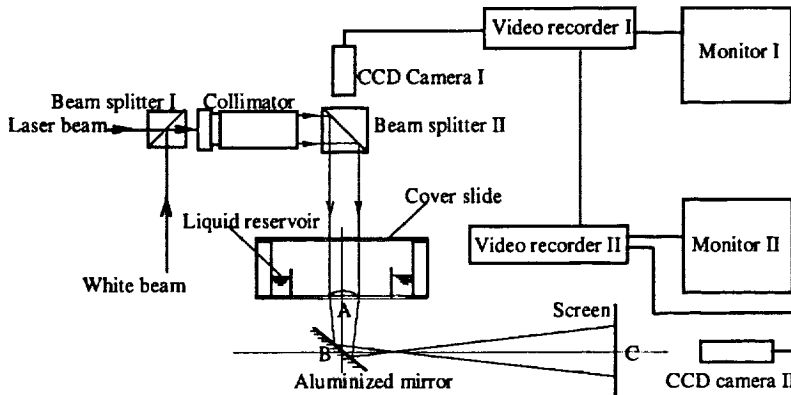


Fig. 1 Schematic of experimental setup

RESULTS AND DISCUSSION

Experimental evidence indicated that evaporation strongly influences the spreading of an R-113 drop. In the saturated vapor environment, the drop is almost completely wetting. The contact diameter of the drop increases monotonically. However, when the drop is placed in a nonsaturated vapor environment of R-113 or simply in open air, the drop becomes partial wetting due to the competition between spreading and evaporation. As predicted by Anderson and Davis [5], the drop undergoes a "weak" evaporation regime where the drop spreads initially, and then a "strong" evaporation regime where the drop contact diameter decreases monotonically in time. The sessile drop placed in the three different vapor environments shows quite different spreading characteristics.

The evolution of contact diameter, d , is directly measured by the top view recorded by the recording system I. The tested drops are relatively small and are not deformed significantly by gravitational effects and therefore, can be considered to be sphere caps with a good approximation [7]. The method developed by Zhang and Yang [13] is used to determine the evolution of the contact angle, θ , and the drop volume, V . By a very simple geometric relationship, the following expressions were derived:

$$\theta = \text{Arc sin } \frac{d}{2R} \quad (1)$$

$$V = \pi h^2 \left(R - \frac{h}{3} \right) \quad (2)$$

Here, h is the maximum height of the sphere cap which is determined by $h = R - \sqrt{R^2 - d^2/4}$, R is the curvature radius of the liquid sphere cap, which can be calculated from $R = (n-1)sd/(D+d)$, where n is the refractive index of the liquid (here it is R-113), s is the distance from the center of the drop contact base via the mirror to the screen, which equals to $AB + BC$ shown in Fig.1, D is the diameter of the outmost fringe ring of the drop refractive image on the screen. The instant evaporation rate, W , can be calculated by the following equation:

instantaneous

$$W = 2\pi rh(R - \frac{h}{3}) + \pi h^2 (\dot{R} - \frac{\dot{h}}{3}) \quad (3)$$

It is obvious that only two basic parameters are needed to measure: the contact diameter, d , and the outmost fringe ring diameter of the drop refractive image, D . In practice, we directly calculate the approximate instant evaporation rate, based on Eq. 2, from $W = \Delta V / \Delta t$, where ΔV is the difference of volumes between the measuring time interval Δt . Figure 2 shows a typical picture of the top view of the drop and its correspondent refractive image on the screen. The pictures were taken at the moment of 1.97 sec. after an R-113 drop of 4 μl was placed on the glass slide surface in open air with the room temperature 24 °C and the relative humidity of 44%. It is interesting that a thermocapillary convective flow occurs in the sessile drop evaporating in open air. It is obviously induced by the evaporation. It should be noted that no any inside flow was detected in the spreading drop when the drop is placed in the saturated vapor environment and in a nonsaturated vapor environment with a lower evaporation rate. The details of the convective flow inside the sessile drops induced by the evaporation are beyond the scope of the present study.

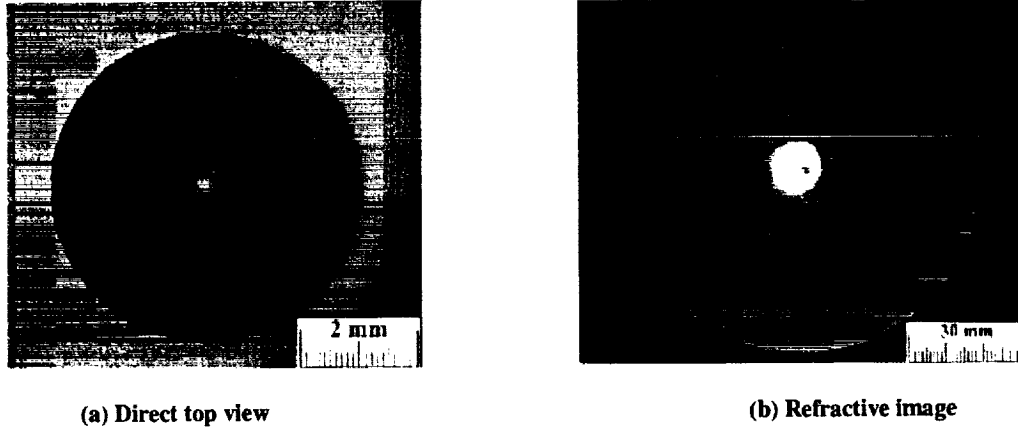


Fig. 2 Typical picture of the top view of a sessile drop and its refractive image

Saturated environment

When an R-113 drop of 2.5 μl is placed on the glass surface in the saturated vapor environment at room temperature 24 °C, it rapidly spreads over the surface. Due to the tendency of complete wetting, the contact diameter of the drop continuously increases and the drop finally becomes a thin “pancake”. The thickness of the wetting film results from a competition between long-range forces and spreading power, which is defined as

$$S = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \quad (4)$$

where γ_{sv} is the surface energy of interface between the solid and the vapor, γ_{sl} and γ_{lv} are the interface tension between the solid and the liquid, and the interface tension between the liquid and the vapor, respectively. As pointed out by Brochard-Wyart et al. [18], the long-range van der Waals forces tends to thicken the film, and the spreading power favors a large wet region. The major spreading process takes place within 1.5 seconds. Figure 3 (a) shows the evolution of the contact diameter, the contact angle, and the volume of the drop. Both the contact diameter and the volume of the drop monotonously increase while the contact angle decreases. It is not strange that the drop volume increases when it spreads out on the glass plate due to condensation of the vapor on the drop surface. The condensation on the whole drop surface obviously promotes the spreading and the condensation at the contact line region plays a crucial role to reduce the surface energy of the vapor-solid interface, γ_{sv} , making the drop completely wetting. The solid surface placed in the saturated vapor environment is certainly moistened, and therefore the physical chemistry properties of the surface are changed, especially the surface energy of the solid surface. It serves the mechanism of the variety of wetting characteristics.

Nonsaturated environment

The most complex and interesting case of this study is the drop spreading under a nonsaturated vapor environment. We tested a drop of 2 μl under the nonsaturated vapor environment at room temperature 24 °C, with an average evaporation rate of 0.032 $\mu\text{l}/\text{sec.}$, which is almost an order of magnitude lower than that the drop evaporating in open air. The evolution of the contact diameter, the contact angle, and the drop volume is shown in Fig.3 (b). The

whole process can be divided to three stages. When an R-113 drop is placed on the glass surface in a nonsaturated vapor environment, the drop rapidly spreads out on the surface first, promoted by condensation of the vapor, just as mentioned above. It is referred as condensation-spreading stage. In fact, condensation and evaporation coexist in this stage. The liquid evaporates upstream from the thick portion of the drop and the vapor condenses near the contact line region. In this first stage, the condensation obviously outweighs the evaporation, and so the volume of the drop increases. When the evaporation dominates the mass transfer between the drop and the vapor environment, both the contact diameter and the drop volume decrease while the contact angle increases, referred as evaporation-retracting stage. The same characteristic of an evaporating sessile drop was actually found in the case of a drop of n-dacane evaporating on polytetrafluoroethylene (PTFE) surface by Bourges-Monnier and Shanahan [8]. They treated this phenomenon as an abnormal evolution and attributed it to slight surface roughness. Actually, this is a normal evolution phenomenon of the volatile sessile drop under the nonsaturated vapor environment with a lower evaporation rate. When evaporation outweighs condensation at the drop surface, the competition between spreading and evaporation makes the drop from spreading to continuous retraction. In the mean time, the contact angle remains at a constant value for a while and then successively increases. When the drop contact diameter retracts to 3 mm the contact angle turns to decrease and the drop contracts more and more rapidly till drying up, referred as rapid contracting stage. In this last stage, the decrease of both the contact diameter and the contact angle is gradually accelerated, though the evaporation rate is slowing down, due to the restrain of geometry relation.

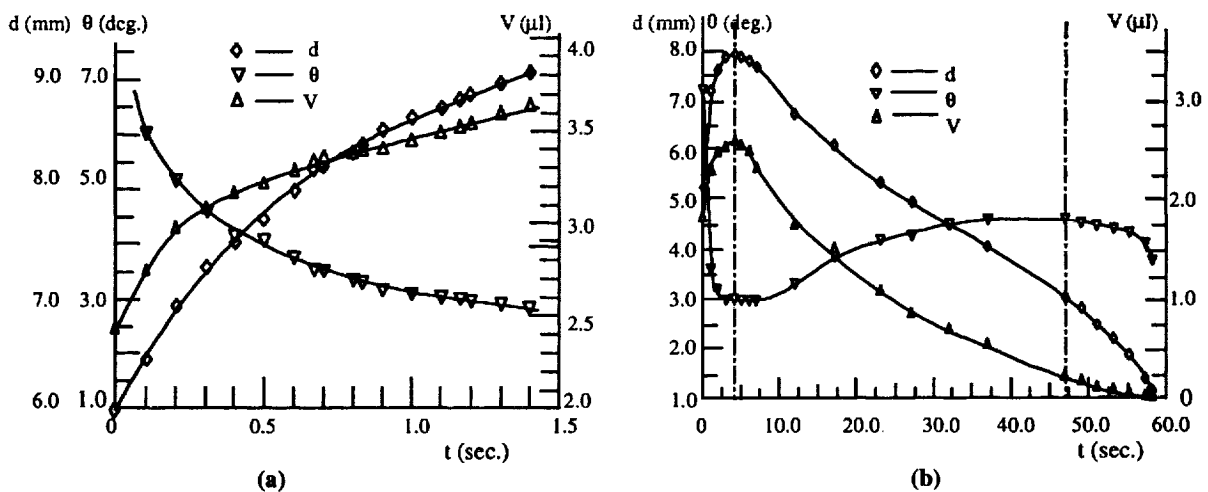


Fig. 3 Evolution of contact diameter, contact angle, and volume of an R-113 sessile drop spreading at (a) saturated vapor environment, and (b) a nonsaturated vapor environment

Open-air environment

An R-113 drop of 4 μl was tested in open-air environment with room temperature 24 °C and relative humidity of 44%. The average evaporation rate is about 0.16 $\mu\text{l}/\text{sec}$. Three stages were also observed, as shown in Fig. 4. In the first stage the competition between spreading and evaporation obviously suppresses the drop spreading and holds the contact diameter to a constant while the contact angle decreases. Then, entering the second stage, the strong evaporation makes the drop to contract linearly with time while the contact angle remains a constant initially and then turns to decrease linearly with time. Finally, same as mentioned in last paragraph, when the drop contact diameter reduces to 3 mm the contraction of the drop is gradually accelerated with a slowing down evaporation rate. It is obvious that the whole evolution process is dominated by the evaporation.

It can be seen that theoretical predictions both in references [5] and [6] are only valid for the nonsaturated environment case with lower evaporation rate. The effects of strong evaporation were undervalued, *underpredicted*.

CONCLUSIONS

Evaporation/condensation plays a crucial role in the spreading of volatile liquid drops and greatly affects the evolution of the contact angle and the contact diameter of the drop. An R-113 drop placed in three different vapor environments presents quite different spreading characteristics. Condensation promotes the spreading, but evaporation suppresses the spreading and favors contraction of the drop. The competition between spreading and a weaker

evaporation results in a complex spreading process with a change in -direction of the evolution of the contact angle and the contact diameter. Strong evaporation can hold back the spreading and pushes the drop to monotonically contract. When the contact diameter of an evaporating sessile liquid drop decreases to 3 mm and less, the contraction of the drop is gradually accelerated till drying up, though the evaporation rate of the drop is slowing down.

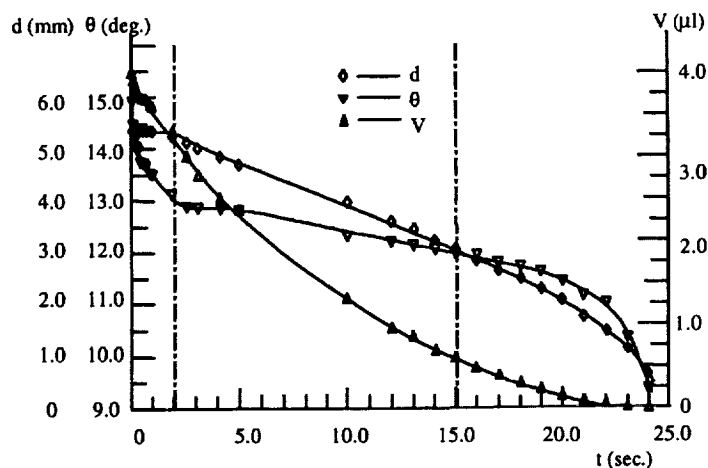


Fig. 4 Evolution of the contact diameter, contact angle, and volume of an R-113 sessile drop spreading in open air with relative humidity of 44%

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